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Electrical characteristics of conjugated self-assembled monolayers in large-area molecular junctions

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We have studied the electrical characteristics of close-packed monolayers of conjugated *para*-phenylene oligomers as a function of molecular length in large-area molecular junctions. An exponential increase in resistance with molecular length is observed, $R \propto \exp(\beta L)$, with $\beta = 0.26 \pm 0.04 \text{ \AA}^{-1}$ and $\beta = 0.20 \pm 0.06 \text{ \AA}^{-1}$ for dithiol and monothiol derivatives, respectively. The decay coefficients are lower than previously determined experimentally using scanning probe or breakjunction techniques. We tentatively explain the low values by the forced planar geometry of the self-assembled molecules. © 2010 American Institute of Physics. [doi:10.1063/1.3503607]

Establishing structure-properties relations is vital for envisioned applications of *Molecular Electronics*. The relationship can be derived from scaling of the resistance with molecular length, yielding information on the transport mechanism as well as on the molecular orbitals involved in the transport. Length dependent transport through molecules has been investigated in various test beds such as breakjunctions and scanning probe techniques.^{1,2} For alkanes, molecules with sp^3 hybridized carbon atoms, it is well-established that off-resonant tunneling is the dominant charge transport mechanism. The resistance (R) increases exponentially with molecular length (L), $R \propto \exp(\beta L)$ with β ranging from 0.38–0.88 \AA^{-1} .²

Studies on various π -conjugated molecules have been performed.^{3–20} The molecules, with delocalized electrons due to sp^2 hybridized carbon atoms, exhibit a smaller energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). For π -conjugated molecules longer than ~ 3 nm hopping conduction was observed.^{12,19,20} For molecules shorter than ~ 3 nm the transport is by tunneling and an exponential dependence of the resistance on molecular length was observed. Values for β range from 0.04–0.61 \AA^{-1} and are significantly lower than for alkanes. Given this large range of β , a further discussion on the relation with molecular geometry is desired. Here, we report systematic measurements of π -conjugated *para*-phenylene oligomers of various lengths using large-area molecular junctions. The technology combines a near 100% yield with high reproducibility and device stability.

The inset of Figure 1 shows a schematic representation of a large-area molecular junction. A self-assembled monolayer (SAM) is formed on a gold bottom electrode inside a photolithographically defined vertical interconnect (via) in photoresist. A conductive polymer, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate), abbreviated as PEDOT:PSS, is spincoated on top of the SAM to fabricate the top electrode. The PEDOT:PSS protects the SAM when an auxiliary gold electrode is thermally evaporated and, thereby, prevents short circuit formation.^{21,22} Using this technique, over 20 000 stable molecular junctions have been fabricated on a 150 mm wafer with a yield of almost unity. This allows for a statistical analysis of the electronic properties. Junctions were fabricated using *para*-phenylene dithiols and monothiols with increasing number of phenylene rings (abbreviated as P1DT–P4DT and P1MT–P3MT). The chemical structures are presented in Tables I and II.

Synthesis of the molecules was performed via prescribed procedures.²³ Monolayers of P1DT–P4DT and P1MT–P3MT were grown from 300 μM SureSeal THF solution in a N_2 glovebox for 36 h. For P3DT and P4DT the acetyl-protected compounds were used which were deprotected during assembly by the addition of two drops of ammonia to 90 ml of SAM solution. SAM formation was checked by variable angle spectroscopic ellipsometry in the spectral range 300–500 nm at angles of incidence 65°, 70°, and 75°. Monolayer thicknesses were determined by modeling the data at all angles and wavelengths using an isotropic refractive index of 1.55, neglecting absorption of the monolayers.

Tables I and II present monolayer thicknesses of P1DT–P4DT and P1MT–P3MT as determined from ellipsometry. These thicknesses are to be compared to the molecular lengths, and fix the maximal layer thickness of the monolayer assuming alignment with the surface normal. The molecular end-to-end distance is calculated with ACD LABORATORIES 11.0 software and 2.3 \AA is added for the Au–S bond. For both series, the layer thicknesses are consistently below

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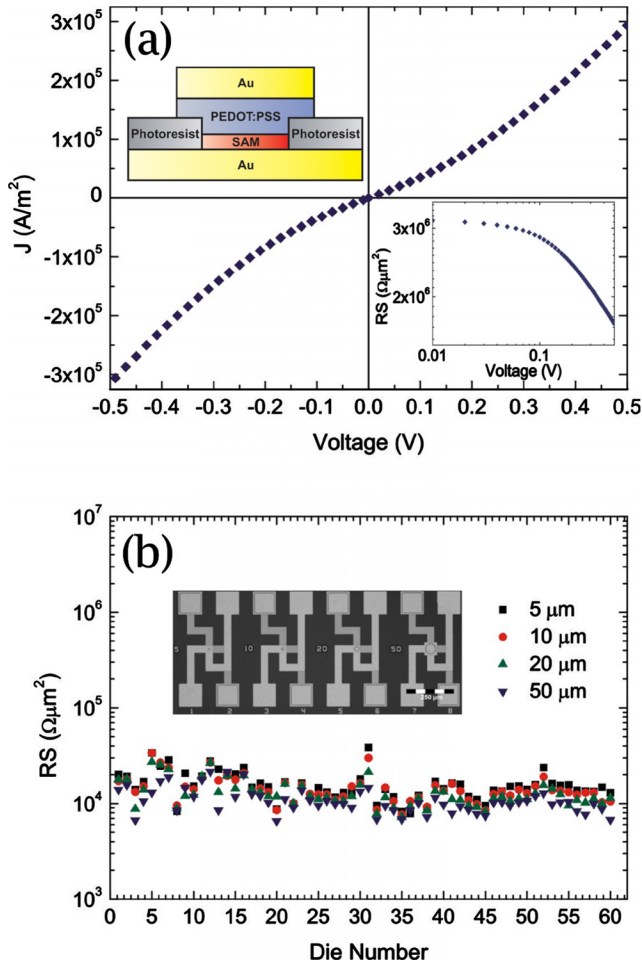


FIG. 1. (Color online) (a) Current density vs voltage (J - V) characteristics of P4DT in large-area molecular junctions. Averaged data from devices with diameters 5–50 μm . Bottom right inset: Replotted RS - V characteristics with a logarithmic voltage axis. Top left inset: Schematic representation of a large-area molecular junction. (b) Statistics of the RS of P1MT in large-area molecular junctions. RS of 240 molecular junctions is shown from 60 dies each containing four junctions with diameter 5, 10, 20, and 50 μm . Inset: Optical micrograph of a die with junctions of diameter 5–50 μm .

the length of a single molecule. This deviation arises from a nonzero tilt angle of the molecules in the layer. The tilt angle decreases with increasing molecular length which is expected for close-packed monolayers. A smaller tilt is favorable to minimize free energy of long molecules because of increased π - π interactions between the phenyl rings. The ellipsometry data of Tables I and II are in agreement with previously published results^{23,24} and establish the formation of close-packed monolayers.

Large-area molecular junctions of the *para*-phenylene

TABLE I. Thicknesses of SAMs of *para*-phenylenedithiol oligomers as determined from ellipsometry measurements.

Molecule	Structure	Molecular Length (\AA)	Monolayer Thickness (\AA)	Tilt Angle (deg)
P1DT		8.9	5.8	49
P2DT		13.3	9.8	43
P3DT		17.6	14.7	33
P4DT		21.8	20.6	17

TABLE II. Thicknesses of SAMs of *para*-phenylenemonothiol oligomers as determined from ellipsometry measurements.

Molecule	Structure	Molecular Length (\AA)	Monolayer Thickness (\AA)	Tilt Angle (deg)
P1MT		7.9	2.4	72
P2MT		12.3	9.6	38
P3MT		16.6	15.7	17

oligomers were characterized as described before.^{21,22} Complete current density versus voltage (J - V) scans were performed on a subset of junctions. Figure 1(a) shows the average J - V characteristics of P4DT. The characteristics are symmetric with respect to bias and are nonlinear; the normalized resistance (RS) is constant at low bias and decreases for higher biases (see inset). Figure 1(b) shows RS values at 0.5 V of P1M as a function of device area and die number. For each oligomer, 62 identical dies with four molecular junctions of diameter 5, 10, 20, and 50 μm were characterized (see inset). The data demonstrate scaling of the resistance with junctions area, as well as the yield and reproducibility of the junctions. Both Figs. 1(a) and 1(b) are representative for all fabricated junctions.

Figure 2 presents RS at 0.5 V bias as a function of molecular length for P1DT–P4DT, P1MT–P3MT and PEDOT:PSS only. Every data point is an average of at least 240 devices with diameters of 5–50 μm . For both series RS increases exponentially with molecular length. The tunneling decay coefficient β equals $0.26 \pm 0.04 \text{ \AA}^{-1}$ for *para*-phenylenedithiols (P1DT–P4DT) and $0.20 \pm 0.06 \text{ \AA}^{-1}$ for *para*-phenylenemonothiols (P1MT–P3MT). By extrapolation of the fit to zero length a contact resistance of $3.5 \times 10^3 \Omega \mu\text{m}^2$ is found. This value coincides with the resistance of junctions without a SAM, i.e., PEDOT:PSS.

A remarkable feature of the data is that the RS for large-area molecular junctions with phenylenes is higher than for similar junctions with alkanes. A possible explanation is a smaller fraction of contacted molecules. However, this effect

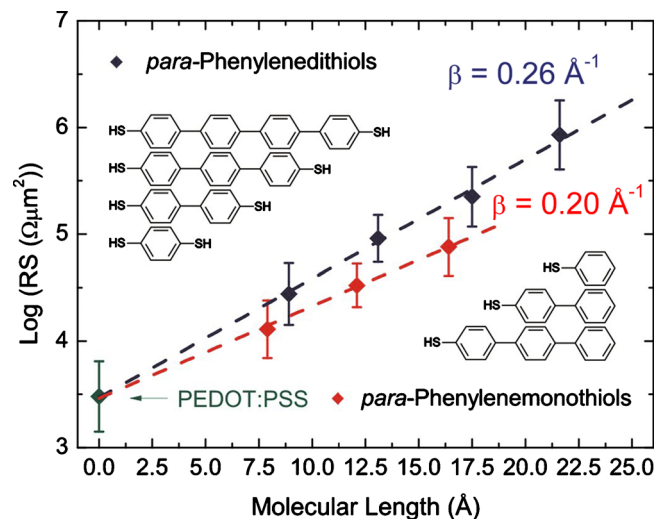


FIG. 2. (Color online) Normalized resistance, RS , as a function of molecular length for P1DT–P4DT and P1MT–P3MT in large-area molecular junctions on a semilogarithmic scale. Every data point is an average of at least 240 devices of 5–50 μm in diameter. Error bars by standard deviation.

can only explain part of the difference. Further investigations in our group aim at understanding of the contact resistance. We note that measuring the length dependence of the molecular conductance represents the most consistent technique to investigate and compare different molecular species.

In fact, the decay coefficients for alkanes have been determined using large-area molecular junctions and found to be 0.66 \AA^{-1} and 0.73 \AA^{-1} for alkanedithiols and alkanemonothiols, respectively.^{21,22} A smaller β is expected for π -conjugated molecules due to their smaller HOMO-LUMO gap, as indeed observed. Therefore, the set of β values shows consistency within the large-area molecular junction geometry. Nevertheless, the β -values found for the phenylenes are lower than reported in literature using single molecules as well as SAMs, i.e., $\beta = 0.35\text{--}0.61 \text{ \AA}^{-1}$.^{3,5–8,10}

To address the relative low values of β , it is interesting to make a comparison with theoretical predictions. Calculations using different formalisms resulted in $\beta = 0.17\text{--}0.51 \text{ \AA}^{-1}$.^{25–33} Kondo *et al.*²⁷ and Liu *et al.*³¹ have studied the influence of the ring torsion angle between the phenyl rings and found β as low as 0.17 and 0.24 \AA^{-1} for planar *para*-phenylene systems, i.e., no torsion angle between adjacent phenyl rings. The experimentally determined coefficients in large-area molecular junctions match closely to these values. The small torsion angle can arise from the closed packing of molecules in the SAM. To reduce intermolecular repulsion and maximize π – π interactions the phenyl rings are forced planar. Increased delocalization over the planar π -conjugated molecule lowers the HOMO-LUMO gap and enhances molecular level broadening, resulting in smaller decay coefficients.^{10,34} We therefore tentatively explain the low coefficients by the influence of the monolayer on the molecular geometry. Single, free molecules are expected to exhibit a nonplanar geometry because of freedom of rotation around the chemical bonds. Therefore smaller coefficients can be expected for monolayer junctions compared to single molecule measurements. The described effect of packing is of minor importance for SAMs of alkanes.

Additional parallel transport levels as well as enhanced level broadening can further reduce β . Possible cooperative effects can account for changes in the electronic structure of the molecules. Specifically, delocalization in the plane of the monolayer by virtue of the π – π interactions between molecules can reduce the HOMO-LUMO gap of molecules.

In summary, we have fabricated large-area molecular junctions containing *para*-phenylene oligomers with an increasing number of phenyl rings. The tunneling decay coefficient β was determined for both series, resulting in $0.26 \pm 0.04 \text{ \AA}^{-1}$ and $0.20 \pm 0.06 \text{ \AA}^{-1}$ for dithiols and monothiols, respectively. The tunneling decay coefficients are lower than reported for π -conjugated molecules but match closely with theoretical calculations assuming a planar molecular geometry. The low torsion angle can arise from self-assembly of the molecules in a close-packed monolayer. The current results possibly show cooperative effects on the charge transport of single molecules in SAMs.

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